

Photoelectron spectroscopy of large (water) $_n^-$  ( $n=50-200$ ) clusters at 4.7 eVAster Kammrath, Jan R. R. Verlet, Graham B. Griffin, and Daniel M. Neumark<sup>a)</sup>*Department of Chemistry, University of California, Berkeley, California 94720**and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

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The hydrated electron  $e_{aq}^-$  has long been a species of considerable interest, studied extensively by both experimental and theoretical methods.<sup>1</sup> Several recent papers have focused on the relation between  $e_{aq}^-$  and its cluster analog,  $(H_2O)_n^-$ ,<sup>2-7</sup> exploring, for example, the connection between the dynamics of the bulk hydrated electron<sup>8</sup> and those of the excess electron in water clusters. A key question underlying this discussion is whether or not the excess electron is solvated internally in the cluster, roughly approximating the bulk situation, or if it is solvated on the surface of the cluster, an issue that arose after early experimental<sup>9</sup> and theoretical<sup>10</sup> studies of these species.

Photoelectron spectra of large anionic water clusters ( $n \leq 200$ ) taken at 3.1 eV in our laboratory revealed two isomers coexisting over a wide range of cluster sizes.<sup>11</sup> Based on our interpretation of the time-resolved dynamics of the two isomers<sup>2,3</sup> and theoretical studies which predicted that a surface-solvated excess electron would have a lower vertical detachment energy<sup>10</sup> (VDE) than an internally bound excess electron, we assigned the less tightly bound isomer (isomer II) to a solvent configuration in which the excess electron is bound on the surface of the water cluster. Further support for this assignment was obtained, indirectly, in studies of the dynamics following charge-transfer to solvent in  $I^-(water)_n$  clusters.<sup>12,13</sup> The more tightly bound isomer (isomer I) was correspondingly assigned to an isomer in which the excess electron is internally solvated.

Recent theoretical work by Turi *et al.*,<sup>14</sup> however, suggested that isomer I may also be a surface state. Their simulation recovered two isomers in the range of  $n=20-200$ . The VDE's for the more weakly bound of their predicted isomers had VDEs that corresponded well to those experimentally determined for isomer II clusters in the size range of  $n=20-66$  but lay between the experimental VDEs for isomers I and II for  $n=104$ .<sup>15</sup> Turi *et al.* correlated this isomer to our isomer I and assigned it to a solvent configuration with the electron solvated on the cluster surface. They assigned the more tightly bound calculated isomer, which they claimed was not seen in our experiment, to an internally solvated electron. In agreement with the earlier work by Barnett *et al.*,<sup>10</sup> they found this theoretically predicted internal state to be more tightly bound than the experimentally determined VDEs of isomer I.

This situation has motivated us to revisit the photoelectron spectroscopy of large water clusters in the range of  $n \leq 200$ , using a significantly higher photon energy of 4.7 eV. This energy exceeds the VDEs predicted for the most tightly

bound isomer by both Barnett *et al.* and Turi *et al.*, so the results presented here check whether more tightly bound water cluster anions were being produced in our experiments but not detached at the lower photon energy (3.1 eV).

The photoelectron imaging experiment and production of water clusters have been described elsewhere.<sup>11</sup> Photoelectron spectra were taken both at “warmer” source conditions (backing pressure of 10–20 psi Ar) found to favor isomer I and at “cooler” source conditions (backing pressure of 30–40 psi Ar) found to favor isomer II. Electrons were detached from the cluster using  $\sim 1$  ps laser pulses at 264 nm ( $\sim 4.7$  eV), produced by frequency tripling the chirped-pulse amplified output of a Ti:sapphire oscillator. Spectra were collected over 80 000–400 000 laser shots, depending on cluster size. Background signal from scattered laser light was compensated for by background subtracting an image with the ion beam blocked, with an equal number of laser shots, from each spectrum.

Representative photoelectron spectra for cluster sizes over the size range of  $n=50-200$  are shown in Fig. 1, with

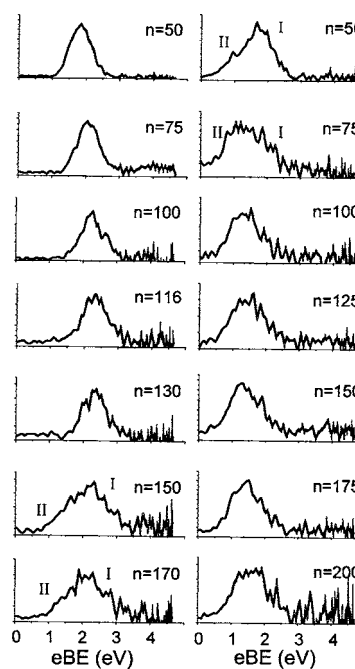


FIG. 1. Representative photoelectron spectra for (water) $_n^-$  clusters with  $n=50-200$ . The left hand column shows data taken at source conditions favoring isomer I; the right hand column shows data taken at source conditions favoring isomer II. Spectra with laser noise subtracted are shown in gray. Black lines show result of smoothing with 20 point adjacent averaging. Roman numerals I and II indicate contributions from both isomers.

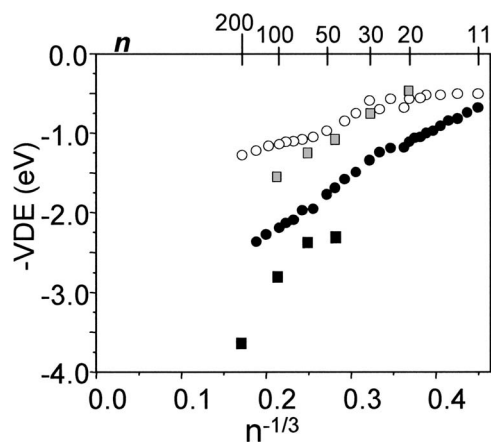


FIG. 2. Vertical detachment energy as a function of inverse cluster radius for (water) $_n^-$  isomer I (black circles) and II (open circles). Black and gray squares are internal and surface bound isomers as calculated in Ref. 14.

spectra taken at source conditions favoring isomer I ( $n = 50-170$ ) shown on the left hand side and those with source conditions favoring isomer II ( $n = 50-200$ ) on the right. All spectra are for (D<sub>2</sub>O) $_n^-$  except those for  $n \geq 150$  under conditions favoring isomer I; these are reported for (H<sub>2</sub>O) $_n^-$ . These choices reflect the fact that (D<sub>2</sub>O) $_n^-$  clusters are generally more easily observed than (H<sub>2</sub>O) $_n^-$  clusters, but we have also found it easier to produce large clusters of isomer I in H<sub>2</sub>O than in D<sub>2</sub>O. Actual spectra (with laser noise subtracted out) are shown in gray. The black lines superimposed are the smoothed spectra obtained by 20 point adjacent averaging of the original spectra. Only two isomers are observed, with vertical detachment energies matching those of isomers I and II previously reported.<sup>11</sup> The broadening observed in the spectra of  $n = 50$  and 75 (on the right) and 150 and 170 (on the left) is most likely due to the presence of both isomers I and II simultaneously in the expansion, as labeled in Fig. 1. Note that there is an even more weakly bound isomer, isomer III, which is only seen for smaller (D<sub>2</sub>O) $_n^-$  clusters than those reported here.<sup>11</sup>

Figure 2 shows experimental negative VDE's of (water) $_n^-$  clusters, shown as black (isomer I) and open (isomer II) circles. The results in Fig. 2 for the largest clusters of both types are new; all other VDE's observed in the current study agree with those previously measured<sup>11</sup> at 3.1 eV. Squares represent the VDE's calculated by Turi *et al.*<sup>14</sup> for internally (black) and surface-solvated (gray) isomers.

There is no indication of an isomer more tightly bound than isomer I for cluster anions with as many as 200 water molecules. Hence, under the conditions of our earlier experiments, we were not producing appreciable amounts of water cluster anions with higher electron binding energies than were accessible at the photon energy used in those experiments. However, our results do not rule out the claim by Turi *et al.*<sup>14</sup> that internally solvated clusters exist with higher VDEs than isomer I clusters, because such clusters may sim-

ply not be produced in sufficient quantity in our ion source for either kinetic or thermodynamic reasons. One could argue that the excess electron is not detached if it is internally solvated in a large cluster but is rather trapped by the surrounding layers of water molecules so that we are unable to observe it. However, in ammonia clusters, the excess electron is generally accepted to reside inside the cluster, yet photodetachment is observed from clusters as large as  $n = 1100$ .<sup>16</sup>

The results presented here do not resolve the controversy regarding surface versus internal solvation but do fill in one of the gaps in our earlier experiments. It will be of interest to extend these experiments to even larger clusters in order to see if new, more strongly bound isomers eventually appear. In addition, experiments in which anions are trapped and collisionally cooled by a low pressure buffer gas are likely to give greater thermodynamic control over cluster populations than is possible under the highly nonequilibrium conditions of a free-jet expansion.

In summary, we have conducted a systematic study of the photoelectron spectra of water anion isomers in the range of  $n = 50-200$  at 4.7 eV. Although this allows us to probe cluster anions with significantly higher binding energies, we do not observe isomers with higher VDEs than those already reported.<sup>9,11</sup>

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